

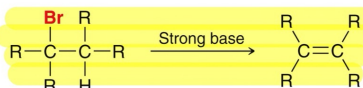
Chapter 7

Preparation of Alkynes

Elimination Reactions of Dihalides

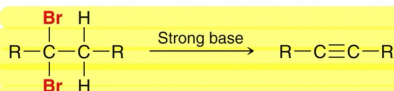
Like alkenes, alkynes can also be prepared by elimination

Need a **dihalide** to make an alkyne



(Section 8.7)

An alkyl halide



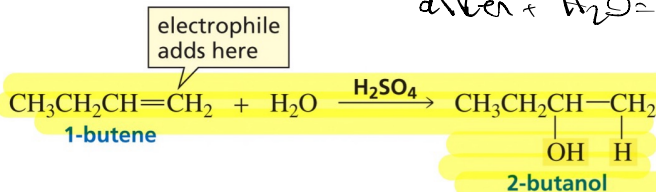
An alkyl dihalide

→ elimination reaction
= halogenin ayrılıp çarku bağa dönməsi

• strong base kullənir

Acid-Catalyzed Addition of Water to an Alkene

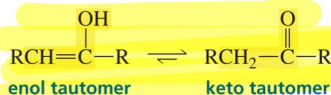
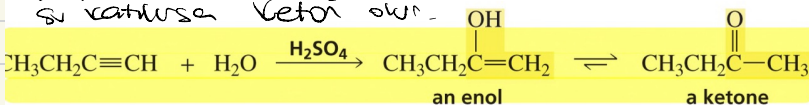
alken + H₂O = alkol



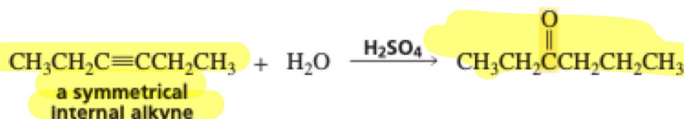
markovnikova göre
eklenir

Acid-Catalyzed Addition of Water to an Alkyne

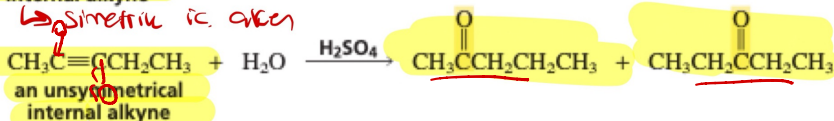
NGT = asetik asit + H₂O = asetik asidin birim ayrılması + asetik asit
su katılınca keton olur



tautomerization

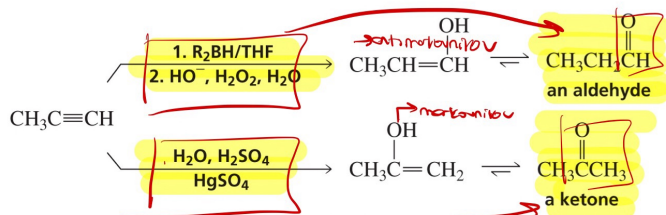
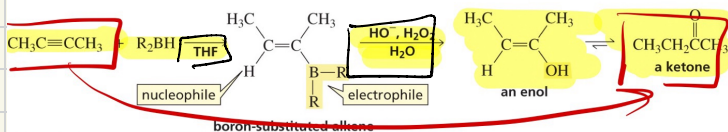


→ simetrik iç alken



→ asimetrik iç alken

Hydroboration-Oxidation

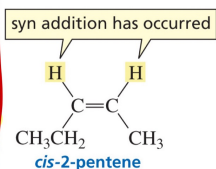
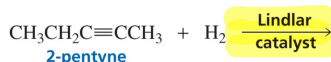
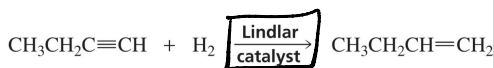


Terminal alkynes form aldehydes.

Internal alkynes form ketones.

ve alkınler aldehit'e dönüşür
iç alkınler ketona dönüşür.

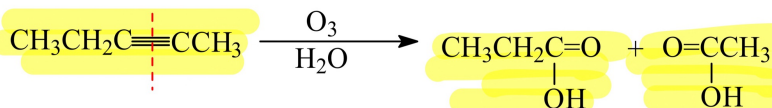
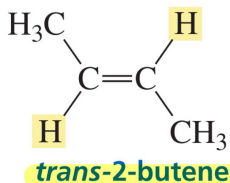
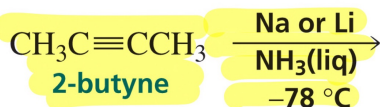
Stopping at the Alkene



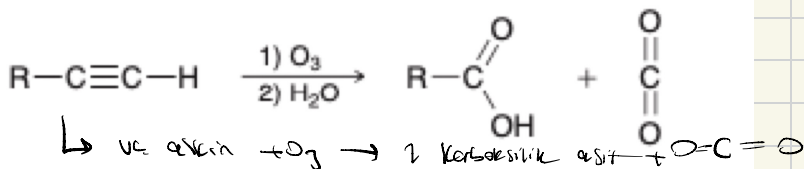
Lindlar \rightarrow cis alkene

Na or Li \rightarrow trans alkene
Nety

Anti Addition

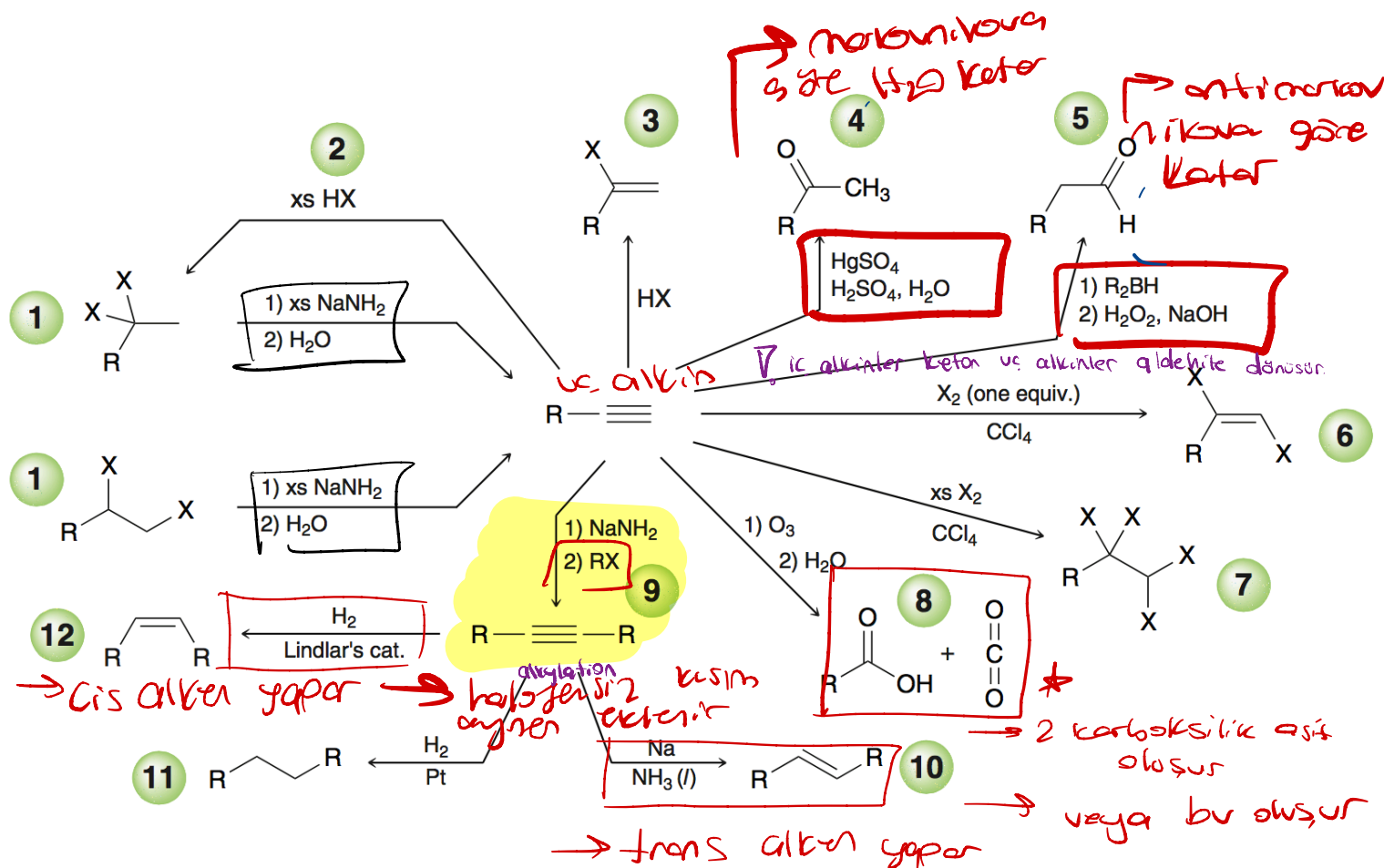


\rightarrow iç alkın + $\text{O}_3 \rightarrow$ 2 farklı karboksilik asit



Reactions of Alkynes - Summary

1. Elimination
2. Hydrohalogenation (two equivalents)
3. Hydrohalogenation (one equivalent)
4. Acid-catalyzed hydration
5. Hydroboration-oxidation
6. Halogenation (one equivalent)
7. Halogenation (two equivalents)
8. Ozonolysis
9. Alkylation
10. Dissolving metal reduction
11. Hydrogenation
12. Hydrogenation with a poisoned catalyst



Chapter 6

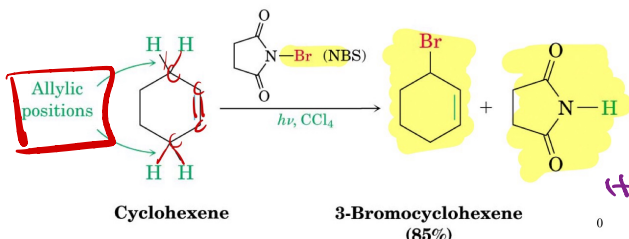
Preparing Alkyl Halides

Allylic Bromination of Alkenes

N-bromosuccinimide (NBS) selectively brominates allylic positions

Requires light for activation

A source of dilute bromine atoms



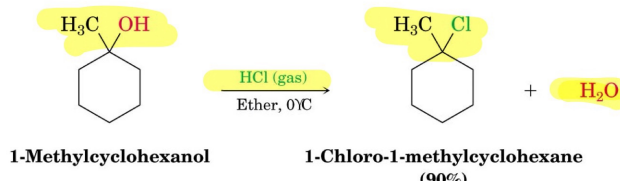
Preparing Alkyl Halides

From Alcohols

Reaction of tertiary C-OH with HX is fast and effective

Add HCl or HBr gas into ether solution of tertiary alcohol

Primary and secondary alcohols react very slowly and often rearrange, so alternative methods are used



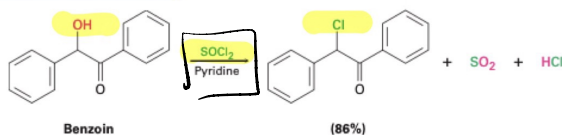
Preparing Alkyl Halides

From Primary and Secondary Alcohols

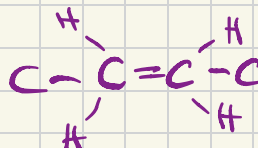
Specific reagents avoid acid and rearrangements of carbon skeleton

Thionyl chloride converts alcohols into alkyl chlorides (SOCl_2 : $\text{ROH} \rightarrow \text{RCl}$)

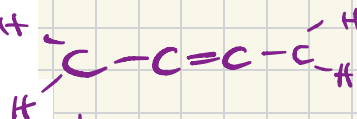
Phosphorus tribromide converts alcohols into alkyl bromides (PBr_3 : $\text{ROH} \rightarrow \text{RBr}$)



\rightarrow vinylic position



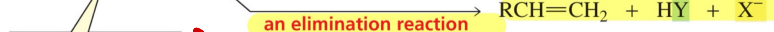
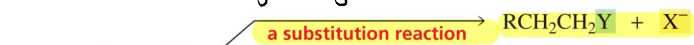
\rightarrow allylic position



per digestion reactions

Substitution reaction—the electrophilic group is replaced by another group. Alkyl halides have **good leaving groups**.

→ yer degistirme reaksiyonu

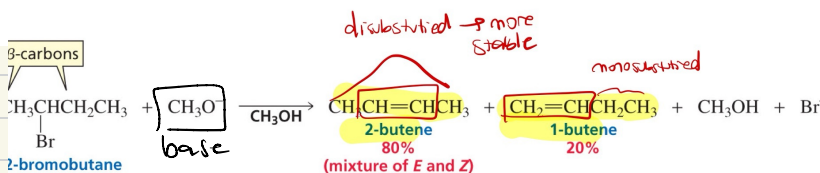
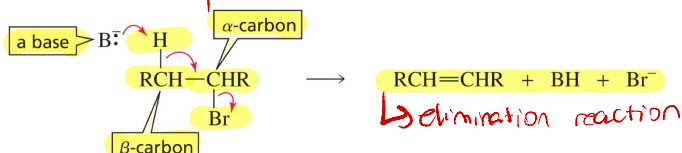


the leaving group

halogen ayrılır ve suda bağlar kurur.

The Halogen Comes off the Alpha Carbon;
the Hydrogen Comes off the Beta Carbon

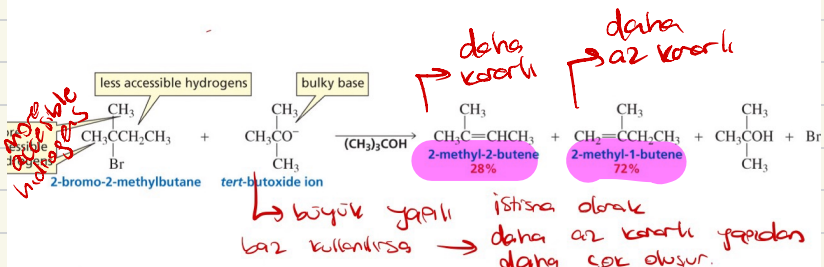
halogenin bağlı olduğu C → α-carbon



The **major product** is the **most stable alkene**.

The **most stable alkene** is (generally) obtained by removing a hydrogen

The More Stable Alkene is Not the Major Product



A **sterically hindered alkyl halide** and a **sterically hindered base** forms the less stable alkene (another exception to Zaitsev's rule).

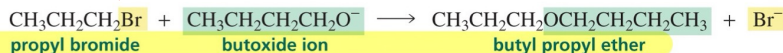
sterik engel = daha çok grubun bağlı olduğu

Williamson ether synthesis

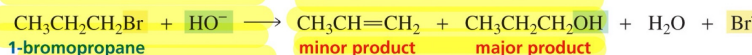
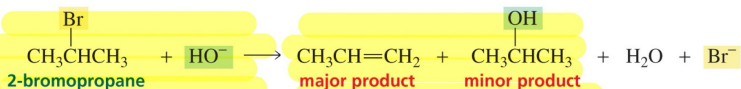


Synthesizing Butyl Propyl Ether

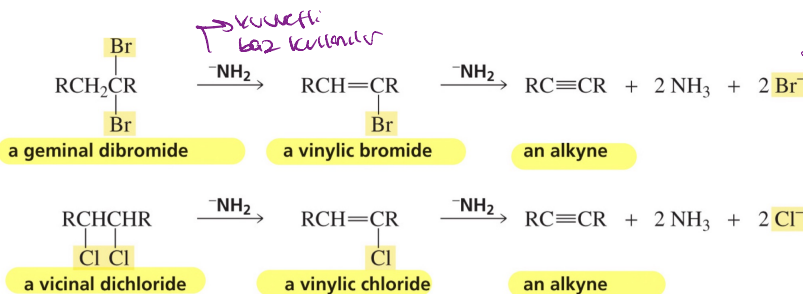
→ halogeni sıkarıp alkil grubunu ayırın etkilem.



Synthesizing an Alkene

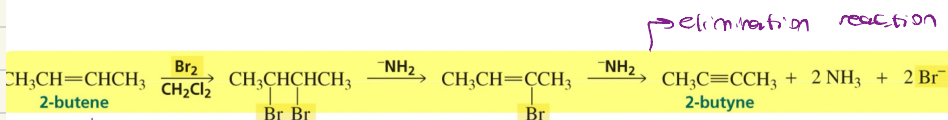


Synthesizing an Alkyne



elimination reaction

Converting an Alkene to an Alkyne



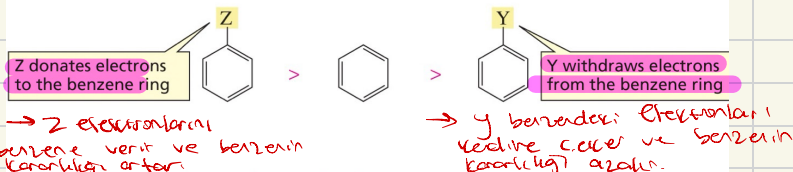
→ ilk Br ekleriz sonra Br'leri kuvvetli bazla kaydırarak 2. Br'yi de ekleriz

chapter 7 son

Chapter 9

The Effect of Substituents on Reactivity

relative rates of electrophilic aromatic substitution



Substituents that donate electron density to the benzene ring increase

benzene's nucleophilicity and stabilize the carbocation intermediate.

Substituents that withdraw electron density to the benzene ring

decrease benzene's nucleophilicity and destabilize the carbocation intermediate.

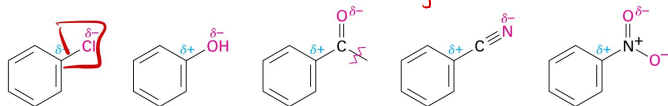
Inductive Effects

groups

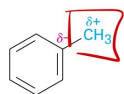
Halogens, C=O, CN, and NO₂ *withdraw* electrons through σ bond connected to ring

Alkyl groups *donate* electrons

Cl, OH, C=O, NO₂, CN elektronları kendine doğru çekerek σ bond ringe bağlar.



Inductive electron withdrawal

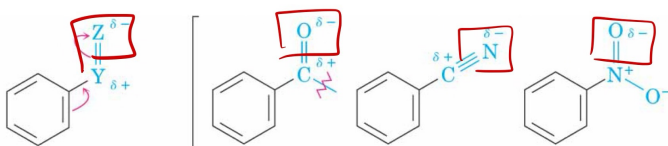


Inductive electron donation

Resonance Effects – Electron Withdrawal

C=O, CN, NO₂ substituents *withdraw* electrons from the aromatic ring by resonance

π electrons flow from the rings to the substituents



Resonance Effects – Electron Donation

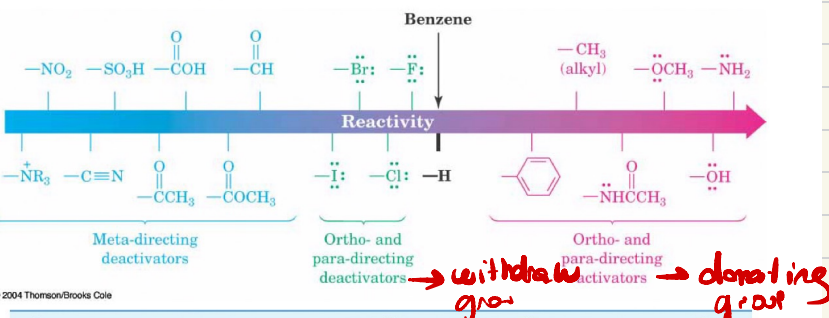
Halogen, OH, alkoxy (OR), and amino substituents *donate* electrons

□ electrons flow from the substituents to the ring

Effect is greatest at ortho and para

Substituent Effects in Aromatic Rings

Substituents can cause a compound to be (much) more or (much) less reactive than benzene

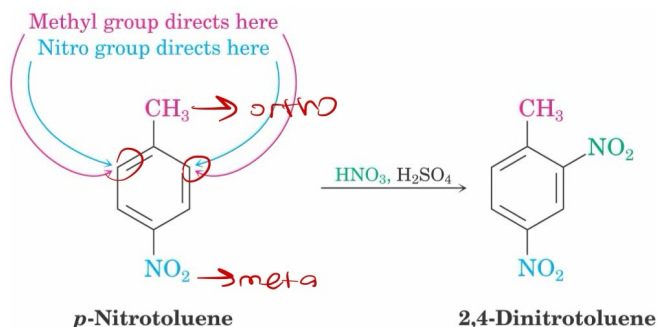


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Substituent	Reactivity	Orienting effect	Inductive effect	Resonance effect
-CH ₃	Activating	Ortho, para	Weak donating	—
-OH, -NH ₂	Activating	Ortho, para	Weak withdrawing	Strong donating
-F, -Cl -Br, -I	Deactivating	Ortho, para	Strong withdrawing	Weak donating
-NO ₂ , -CN, -CHO, -CO ₂ R -COR, -CO ₂ H	Deactivating	Meta	Strong withdrawing	Strong withdrawing

Trisubstituted Benzenes: Additivity of Effects

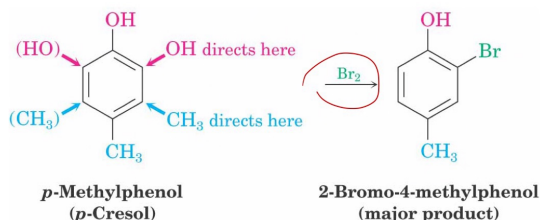
- If the directing effects of the two groups are the same, the result is additive



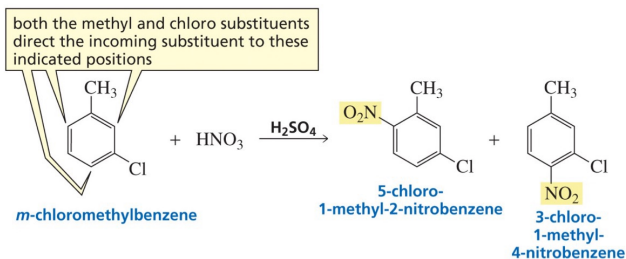
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Substituents with Opposite Effects

- If the directing effects of two groups oppose each other, the more powerful activating group decides the principal outcome
- Usually gives mixtures of products



The Synthesis of Trisubstituted Benzenes

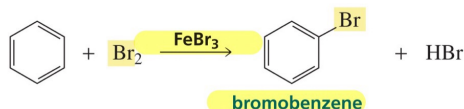


Both substituents direct to equivalent positions.

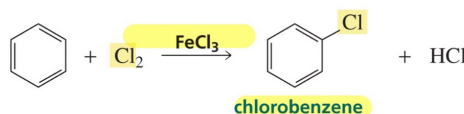
Addition between two substituents is a minor product because of steric hindrance.

Halogenation of Benzene

bromination



chlorination



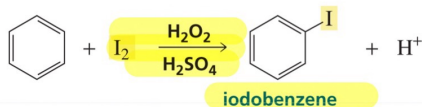
Bromination or chlorination of benzene requires a Lewis acid catalyst because benzene's aromaticity causes it to be less reactive than an alkene.

Ferric bromide (FeBr₃) or ferric chloride (FeCl₃) is usually used

(Br, Cl)
benzene halogenation:
Lewis acid catalysts:
(FeBr₃, FeCl₃)

Iodination of Benzene

iodination



The electrophile is generated differently.

generation of the electrophile



Hydrogen peroxide is commonly used as the oxidizing agent.

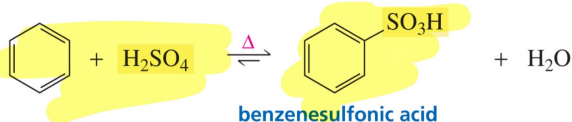
Nitration of Benzene

nitration



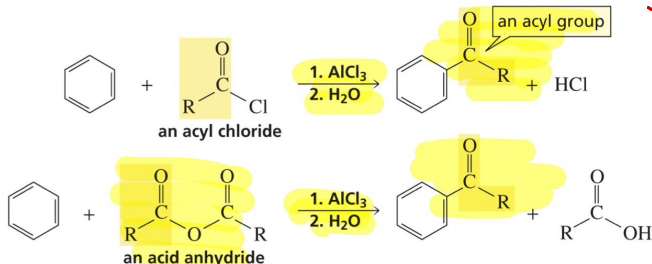
Sulfonation of Benzene

sulfonation



Friedel-Crafts Acylation

Friedel-Crafts acylation



An acyl chloride or an acid anhydride is the source of the acyl group.

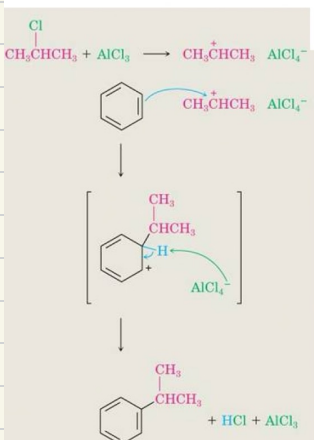
A Lewis acid (AlCl_3) is required.

benzene I₂ H₂O₂ eklenmesi H₂O katalizöründe

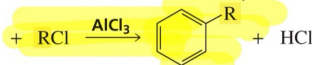
benzene nitrat ve sülfat eklenmesi asit + H₂O olarak gerçekleşir. sülfat.

asil grubu eklenmesi Lewis asit (AlCl₃) katalizöründe

Friedel-Crafts Alkylation



ation



an alkyl group

An alkyl halide is the source of the alkyl group.

A Lewis acid (AlCl_3) is required.

NOT = reaksiyon için alkil halojenürler

Kullanılır Ama aryl halojenür ve vinylik halojenür kullanılmaz.

alkil grubu eklenmesi!
Lewis asit katalizörüdür!
(AlCl_3)

Limitations of the Friedel-Crafts Alkylation

Only alkyl halides can be used (F, Cl, I, Br)

Aryl halides and vinylic halides do not react (their carbocations are too hard to form)

Will not work with rings containing an amino group substituent or a strongly electron-withdrawing group

An aryl halide



A vinylic halide

NOT reactive

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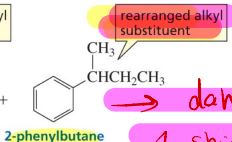
NO reaction

where $\text{Y} = -\text{NR}_3^+, -\text{NO}_2, -\text{CN}, -\text{SO}_3\text{H}, -\text{CHO}, -\text{COCH}_3, -\text{CO}_2\text{H}, -\text{CO}_2\text{CH}_3$

0

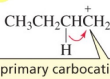
Carbocation Rearrangement Leads to an Undesired Product

Friedel-Crafts alkylation

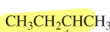


→ daha kararlı olmak için 1 shift yapar

rearrangement of the carbocation

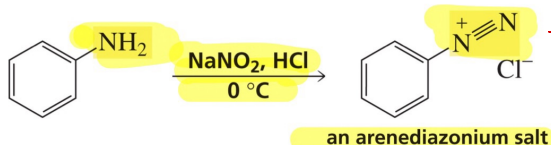


1,2-hydride shift



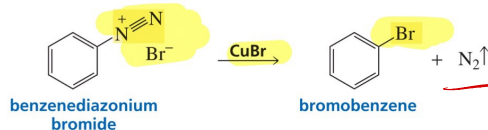
a secondary carbocation

The Synthesis of Substituted Benzenes Using Arene Diazonium Salts

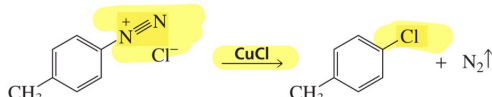


1. aşama arene diazonium tuzudur.

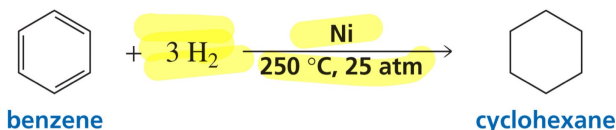
Sandmeyer Reactions



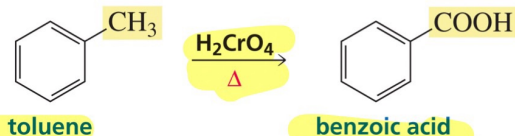
2. aşama Sandmeyer reaction ile (CuBr ve CuCl) kullanılarak benzen halogen üretilebilir.



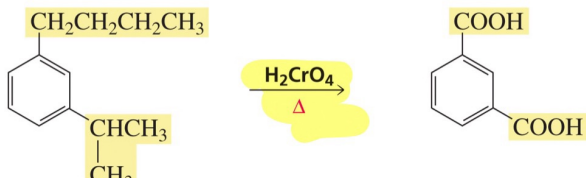
The Benzene Ring is Reduced Only at High Temperature and Pressure



Alkyl Substituents are Oxidized to Carboxyl Groups

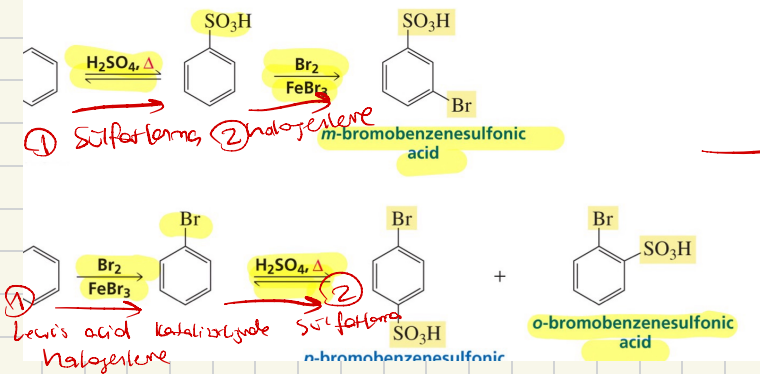


alkil grupları karboksilik asitlere dönüşebilir H₂CrO₄ katalizasyonu



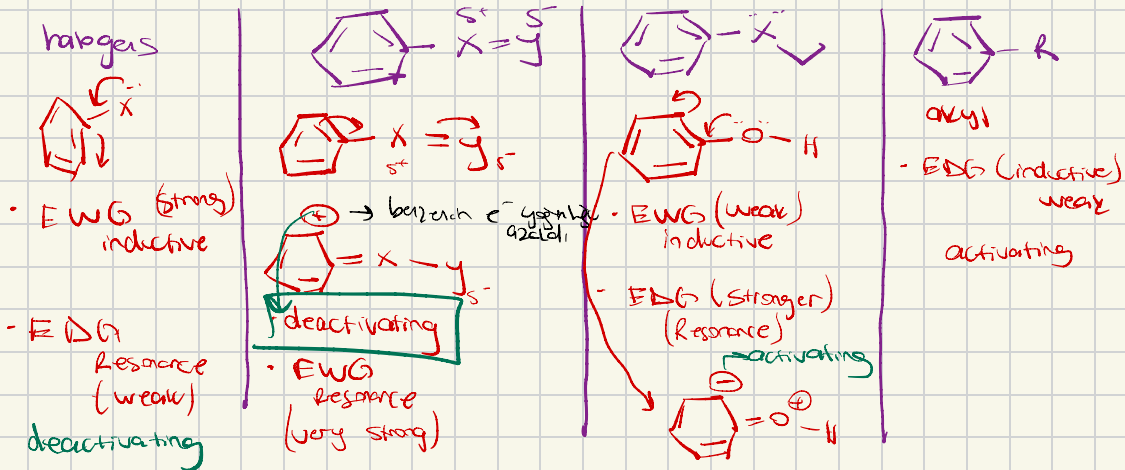
The Order of the Reactions is Important

The order of the reactions is important.

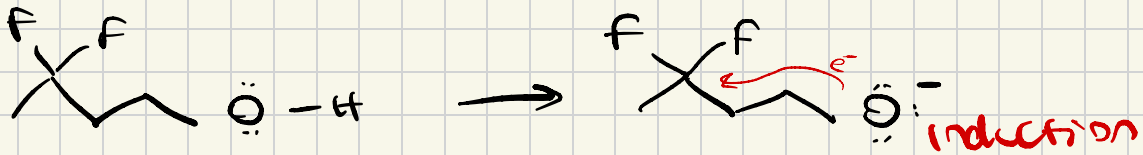
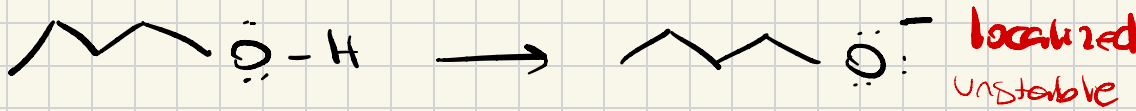


chapter 9 son

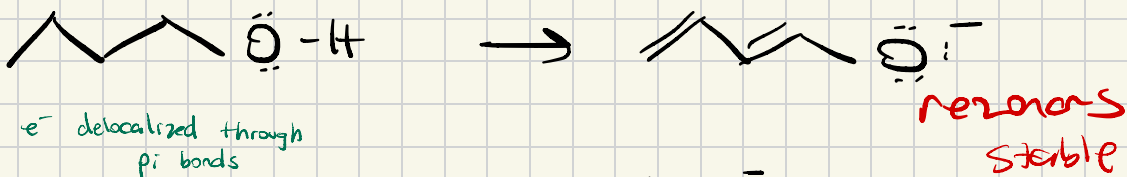
Electrophilic substitution of benzene derivatives



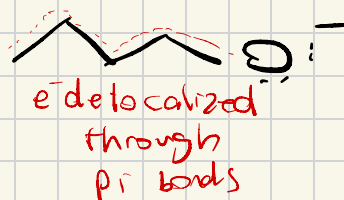
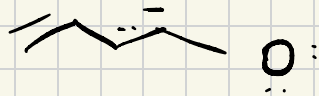
Induction vs Resonance



$\rightarrow e^-$ delocalized through sigma bonds



$\rightarrow e^-$ delocalized through pi bonds



NOT = - yük delocalized olur
 tüm zince dağıldığı için
 more stable olur.

EDG electron donating group, bağlı olduğu karbon atomu aracılığıyla bir moleküldeki elektron yoğunluğunu artırır.
 * nükleofilleri daha güçlü hale getirir.
 \rightarrow Lewis bazı

EWG electron withdrawing group, rezonans veya indüktif etkilerle karışık atomlardan kendisine doğru elektron yoğunluğunu çeker gruplar.

RESONANCE effects are those that occur through the pi system and can be represented by resonance structures. These can be either electron donating (e.g. -OCH₃) where pi electrons are pushed toward the arene or electron withdrawing (e.g. -C=O) where pi electrons are drawn away from the arene.

INDUCTIVE effects are those that occur through the sigma system due to electronegativity effects. These too can be either electron donating electron donating (e.g. -Me) where sigma electrons are pushed toward the arene or electron withdrawing (e.g. -CF₃, +NR₃) where sigma electrons are drawn away from the arene.

A simplified approach to understanding substituent effects is provided, based on the "isolated molecule approach". The text (as do most others) uses the *more rigorous approach* of drawing the resonance structures for each of the intermediate carbocations formed by attack at each of the o-, m- and p- positions and looking at how the initial substituent influences the stability of the system.

We are going to break down the types of substituents into various subgroups based on the structural features of the substituent immediately adjacent to the aromatic ring:

- **type 1 = substituents with lone pairs** (e.g. -OCH₃, -NH₂) on the atoms adjacent to the pi system.
- **type 2 = substituents** that are CH systems (i.e. -alkyl, -vinyl or -aryl).
- **type 3 = substituents** that are C=C systems (i.e. -vinyl or -aryl).
- **type 4 = substituents with π bonds to electronegative atoms** (e.g. -C=O, -CF₃, -NO₂)
- **type 5 = substituents with several bonds to electronegative atoms** (e.g. -CF₃)
- **type 6 = substituents that are halogen systems** (i.e. -F, -Cl, -Br, -I)

Most Activating	
$\text{--}\ddot{\text{O}}\text{--}$	Strongly Activating
$\text{--}\text{NR}_2$	
$\text{--}\text{NH}_2$	
$\text{--}\text{OH}$	
$\text{--}\text{OR}$	
Activating	Moderately Activating
EDG	
$\text{--}\text{NHCR}$	
$\text{--}\text{OCOR}$	
$\text{--}\text{R}$	
Weakly Activating	Weakly Deactivating
$\text{--}\text{C}=\text{CR}_2$	
Reference	Weakly Deactivating
$\text{--}\text{H}$	
$\text{--}\text{X}$	Moderately Deactivating
$\text{--}\text{CH}$	
$\text{--}\text{CR}$	Moderately Deactivating
$\text{--}\text{COR}$	
$\text{--}\text{COH}$	Strongly Deactivating
$\text{--}\text{CCl}$	
$\text{--}\text{CF}_3$	Strongly Deactivating
$\text{--}\text{C}\equiv\text{N}$	
$\text{--}\text{SiOH}$	Strongly Deactivating
$\text{--}\text{NH}_3^+$	
$\text{--}\text{NR}_3^+$	Strongly Deactivating
$\text{--}\text{N}^+\text{--O}^-$	
Most Deactivating	

These effects are a combination of **RESONANCE** and **INDUCTIVE** effects (see [next page](#))
The effects are also important in other reactions and properties (e.g. acidity of the substituted benzoic acids).

Here are some **general pointers** for recognising the substituent effects:

- The **H** atom is the standard and is regarded as having no effect.
- **Activating** groups increase the rate
- **Deactivating** groups decrease the rate
- **EDG = electron donating group**
- **EDG** can be recognised by lone pairs on the atom adjacent to the π system, eg: -OCH₃
- **except** -R, -Ar or -vinyl (hyperconjugation, π electrons)
- **EWG = electron withdrawing group**
- **EWG** can be recognised *either* by the atom adjacent to the π system having several bonds to more electronegative atoms, or, having a formal +ve or δ +ve charge, eg: -CO₂R, -NO₂
- **EDG / activating groups direct ortho / para**
- **EWG / deactivating groups direct meta**
- **except** halogens (-X) which are deactivating **BUT** direct ortho / para
- **EDG** add electron density to the π system making it **more nucleophilic**
- **EWG** remove electron density from the π system making it **less nucleophilic**.